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## Carbon mineral storage in seawater: *Ikaite* ( $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ) columns in Greenland

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### Abstract

The marine Ikka Fjord in Greenland is well known for its remarkable submarine columns made of the cold-carbonate *ikaite* ( $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ). Here, natural processes lead to fast-precipitating ikaite at low temperatures ( $< 10^\circ\text{C}$ ) when carbonate-bearing groundwater seeps through fractures in Ikka Fjord and mixes with seawater. Within an area of  $0.75 \text{ km}^2$ , 678 columns of 1 – 20 meters height have been registered, continuously growing at rates measured at 50 cm per year. Understanding this natural system is of importance for carbon capture and storage efforts as it represents a very efficient method for carbon mineral storage in cold seawater.

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**Keywords:** Ikaite, carbon mineral storage, seawater, low temperature, calcite inhibitors, cyanobacteria, biofilm

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### 1. Introduction

Ikka Fjord in southwest Greenland (Fig. 1) has been subject to extensive research since 1995 due to the presence of close to a thousand submarine columns in the shallow inner part of the fjord. The tallest of these structures are 18–20 m high and have an average diameter of 0.5–1 m. (Fig. 2). At low tide the tips of the tallest columns can be seen

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through the water surface as massive white structures. Being striking statuesque features, the columns were described by the Inuit as “frozen Norse people”, evoking the memory of the Norse who lived in Ikka Fjord in the Late Middle Age and who were drowned after being chased out on the ice during a conflict with the Inuit [1]. Pauly was the first to publish a scientific description of the columns [2] and to also identify that the columns were made of a new mineral *ikaite* ( $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ). This first discovery of natural ikaite has since been followed by a number of other findings in marine, lacustrine, estuarine, and freshwater environments, at near-zero temperatures. The most recent discoveries concern ikaite growth in sea ice in the Arctic, and around Antarctica [3,4] and represent the first discovery of a calcium carbonate phase in sea ice. Ikaite is a metastable phase at all conditions found on Earth [5] and is observed to break down into other hydrous and anhydrous  $\text{CaCO}_3$  phases when it is destabilized by dehydration, i.e. through heating [6,7,8].

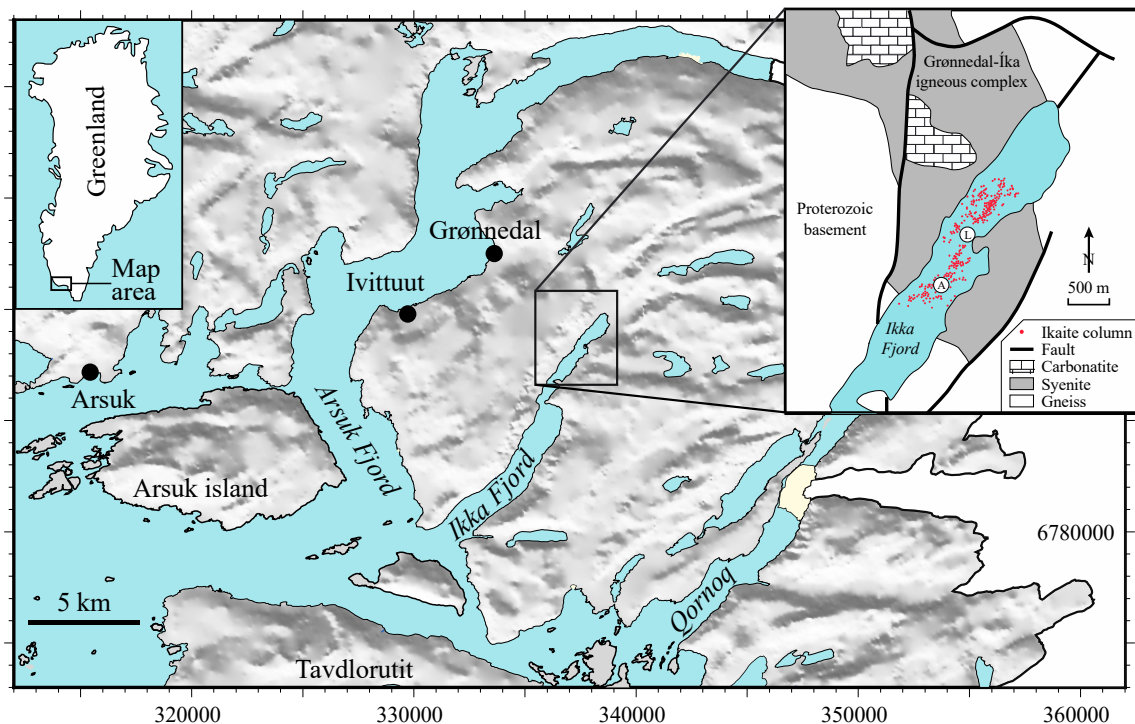


Fig. 1. Map of the Ivittuut area in southwest Greenland with zoom in on Ikka Fjord where all red dots mark the ikaite columns, and A and L mark locations where groundwater was sampled by drilling syringes into the columns. Modified from Stockmann et al. [9].

Thus far the research carried out in Ikka Fjord and its surroundings has focused on: the formation mechanism of the ikaite columns; their distribution within the fjord; and the description of the remarkable biological life that inhabits both the exterior and interior of the column structures as seen in Fig. 2. Recently, new research, within the project presented here and building on the studies of natural ikaite deposits, has begun exploring the potential of ikaite precipitation as a method for carbon mineral sequestration. The natural system of ikaite precipitation in Ikka Fjord takes place in seawater at low temperatures ( $< 10^\circ\text{C}$ ) and very high precipitation rates. This suggests that such a process could be developed into a low temperature carbon mineral sequestration method: an attractive prospect from an energy and resource point of view. No external heating is required during ikaite formation, which in fact is most effective in cold seawater. When ikaite becomes unstable, more stable calcium carbonate phases are formed with no net loss of carbon.

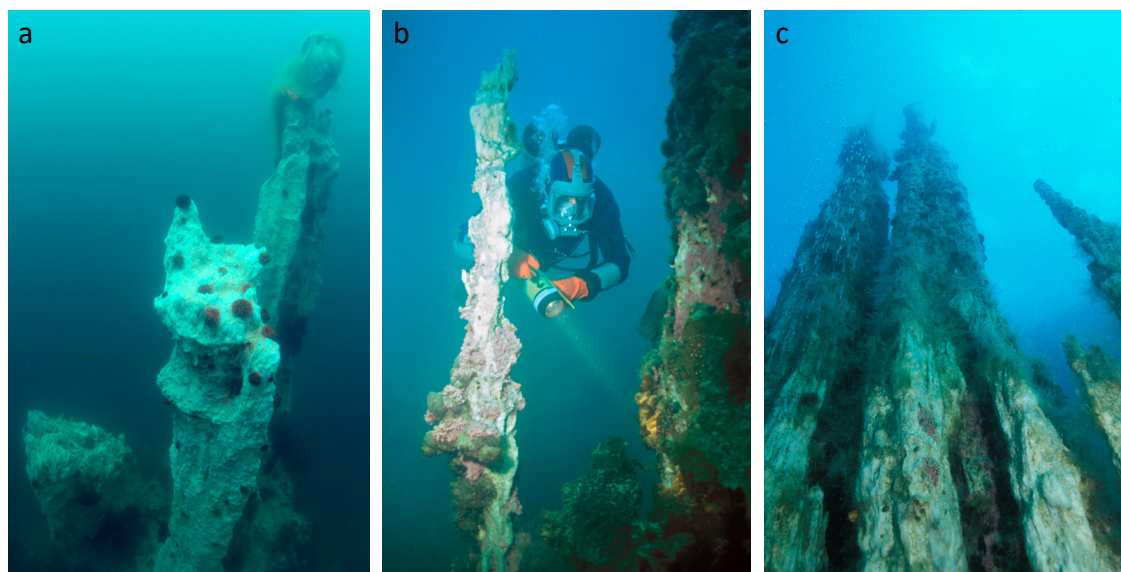


Fig. 2. Photos: Richard Martin. Ikaite columns in Ikka Fjord, SW Greenland (a) “the Viking helmet” column; (b) a diver for scale between a smaller column and one of the 20 m tall columns; (c) “The Twin Towers”, a cluster of 18-20 m tall columns.

## 2. Methods and materials

Since the beginning of the “Ikka project” in 1995, around 10 scientific expeditions to Ikka Fjord have taken place with participation of biologists, geophysicists, geographers and geologists. In addition, divers have played an important part as most of the fieldwork was carried out under water around the columns. With the help of the divers, pieces of columns and specimens of the macro fauna and flora that inhabit the columns were sampled. Selected columns and their interior environment were monitored for pH,  $O_2$  and salinity over longer time periods by electrodes drilled into the columns. Short-term *in situ* profiling and diurnal measurements assessing the internal dynamics of physicochemical parameters,  $O_2$ , pH and light combined with photosynthetic activity measurements revealed a very active endolithic phototrophic community situated in gradients of extreme microenvironmental conditions. The divers also managed to drill syringes into the columns, to extract fluid from their interiors. The column fluids were measured for pH, temperature, salinity and alkalinity immediately after the divers brought them on land. Seawater samples from different depths in the water column were also sampled and measured for comparison.

Different geophysical methods (echo-sounder bathymetry, side-scan sonar imagery and pinger sub-bottom profiling) were employed in the early years of the Ikka project in order to map out and count the column growths in Ikka Fjord. Whilst some 678 individual columns were mapped, these represent only those resolvable in the geophysical data and many more are known to exist from diver-made observations. Nevertheless, these early maps gave insight into the spatial distributions of the columns on the fjord-bed, and suggested that their distribution is governed by certain features in the fjord such as their proximity to the Grønnedal-Íka igneous complex, the bedrock fracture systems and the sedimentary cover over the bed of the fjord.

Bacteria, enzymes, algae and DNA were extracted from the collected column pieces following the fieldwork phases. Also, a large number of cyanobacteria and diatom isolates were obtained from collected ikaite material, and kept in cultures. Molecular work on environmental samples obtained at various depths into the walls of ikaite columns showed distinct zonation of different phototrophic groups. Stratification of phototrophs, diatoms and cyanobacteria, was further confirmed and resolved by fluorescence imaging of specific functional marker pigments on column cross sections. Scanning Electron Microscopy (SEM) imaging of ikaite material containing phototrophic microbes showed a large amount of exopolymeric substances (EPS), adhering phototrophs and ikaite crystal together in the column matrix.

Water samples from numerous springs surrounding Ikka Fjord and lakes located within the Grønnedal-Íka igneous complex (Fig. 1) were collected and measured *in situ* for pH, temperature and conductivity. Furthermore, all fluids

sampled from the columns, seawater, springs and lakes were analyzed for major cations and anions,  $\delta^{18}\text{O}$ , and  $\delta\text{D}$ , and selected samples for  $^{87}\text{Sr}/^{86}\text{Sr}$ . Isotopic studies of the ikaite column samples included  $\delta^{18}\text{O}$ ,  $\delta\text{D}$ ,  $\delta^{13}\text{C}$ , and  $^{14}\text{C}$  for dating.

Representative rock samples of carbonatites and nepheline syenites from the Grønndal-Íka igneous complex (Fig. 1) were collected both from surface exposures and from drill cores taken in 1950 by Kryolitselskabet Øresund A/S. Thin and thick sections were prepared from these samples and studied with the aim of identifying and characterizing the fluid-rock reactions that take place within the complex. Petrographic information was acquired by conventional and cathodoluminescence microscopy. Major and trace element chemistry of calcite, siderite, magnetite and ankerite in the carbonatite samples was determined *in situ* by electron-probe microanalysis (EPMA) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

Finally, a series of laboratory experiments were carried out to simulate the ikaite precipitation that is taking place in Ikka Fjord and to determine the geochemical parameters that control ikaite precipitation. The design of these experiments is shown in Fig. 3 with mixing of two solutions in equal volumes at a specific flow rate. One solution carried 0.03 M  $\text{CaCl}_2$  or seawater of different sources, either natural or synthetic, whereas the other solution contained 0.1 M  $\text{NaHCO}_3$  and 0.1 M  $\text{Na}_2\text{CO}_3$  in different ratios leading to pH 9.9–10.6 (20°C). Identical experiments were carried out at 5, 10, 15 and 20°C to determine the upper temperature limit for ikaite formation. The remainder of the experiments were carried out at 5°C either by use of cooling baths or in a 5°C cooling room. Precipitates from the mixed solution were analysed by X-ray diffraction (XRD) for mineral identification, and Rietveld analysis were applied to all XRD results to obtain quantitative numbers for the phases present.

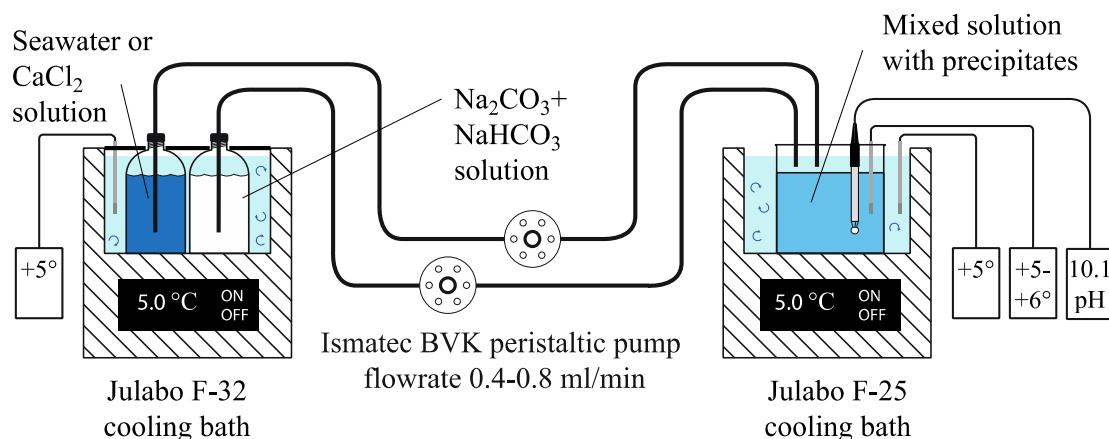


Fig. 3. Experimental setup for the ikaite precipitation experiments using cooling baths. Modified from Stockmann et al. [9].

### 3. Results and discussion

Pauly, in his 1963 paper, had already suggested that the ikaite columns formed over carbonate-bearing springs issuing from the bottom of Ikka Fjord and that they were closely correlated with the outcrops of the Grønndal-Íka igneous complex [2] as seen in Fig. 1. This alkaline complex belongs to a suite of rocks associated with the continental breakup of South Greenland, also known as the Gardar Rifting Event (GRE), at approximately 1300–1100 Ma [10,11]. The complex comprises mainly nepheline syenites in two outer rings, and Ca- and Fe-rich carbonatites in a central plug, which were later cut by several dikes and exposed to faulting, but has otherwise not endured any major tectonic or metamorphic alteration [11]. Seaman and Buchardt reported finding 678 columns taller than 1 m, and an unknown number of smaller columns, in an area of 0.75 km<sup>2</sup>, more or less within the borders of the Grønndal-Íka igneous complex and preferentially following fracture zones in the fjord [12]. The isotopic studies of the fluid extracted from the columns and the ikaite pieces confirmed the theories of Pauly [2]. The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of the column fluids matches the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of meteoric water falling on top of the 500 m tall Grønndal-Íka igneous complex. This suggests that meteoric water percolates from the top of the Grønndal-Íka igneous complex through highly

fractured nepheline syenitic and carbonatitic rocks, undergoing water-rock interactions and creating the groundwater that seeps up through fractures in the Ikka Fjord seabed [13,14]. This groundwater, as extracted from the columns, was shown to have a low salinity of 9, a high alkalinity of 121–179 meq/kg, and a high pH of 10.2–10.5 at *in situ* temperature [13,14]. The column water has a high concentration of  $\text{Na}^+$ , whereas concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{SiO}_2$  and all other major anions were low. Selected results are listed in Table 1 together with the chemical analysis results of seawater and spring water from Ikka Fjord.

Table 1. Chemistry of spring water, groundwater and seawater from Ikka Fjord. Modified from Buchardt et al. [14].

	Spring water, carbonatite	Groundwater from columns	Seawater
Temperature ( $^{\circ}\text{C}$ )	4.2	3.6	4.0
pH ( <i>in situ</i> T)	8.2	10.2 – 10.5	8.1
Salinity	0	9	32.5
Alkalinity (meq/kg)	2.4	121 – 179	2.1
$\text{Na}^+$ (mmol/kg)	0.11	198	437
$\text{Ca}^{2+}$ (mmol/kg)	0.96	0.17	8.83
$\text{Mg}^{2+}$ (mmol/kg)	0.14	1.69	45.7
$\text{SiO}_2$ (mmol/kg)	0.054	b.d.	0.02
$\text{Sr}^{2+}$ (mmol/kg)	0.029	0.007	0.1
$\sigma\text{-PO}_4^{3-}$ (mmol/kg)	b.d.	0.09 – 0.26	0.0001
$\delta\text{D}^{\text{‰}}$ , VSMOW	-97.3	-95.7	-14.2
$\delta^{18}\text{O}^{\text{‰}}$ , VSMOW	-13.10	-13.42	-1.13
$^{87}\text{Sr}/^{86}\text{Sr}$		0.7029*	0.7092

b.d.: below detection, \*calculated for seawater-uncontaminated groundwater in Buchardt et al. [14].

The measured  $^{14}\text{C}$  activity of the ikaite column pieces was low (13–17% modern) and assumed to stem from biological material inside the columns. In combination with the high alkalinity of the groundwater, this led to the conclusion that the carbonate ions entering the ikaite structure originate from dissolving carbonatites in the Grønneðal-Íka igneous complex [13,14]. These carbonatites are to a large extent søvites, i.e. coarse-grained calcite-dominated carbonatites, but in certain areas also seen to be unusually Fe-rich with siderite and ankerite present [11,15,16]. As the column groundwater was observed to be enriched in  $\text{Na}^+$  and carbonate, but contain only very low concentrations of  $\text{Ca}^{2+}$ , new studies are now looking into the fluid-rock reactions in the Grønneðal-Íka igneous complex to explain the chemistry of this groundwater.

The  $^{87}\text{Sr}/^{86}\text{Sr}$  value of ikaite (0.70916) is very close to the  $^{87}\text{Sr}/^{86}\text{Sr}$  value of seawater (Table 1), and very different from those of the carbonatites (e.g., 0.70286). Hence, a seawater source was suggested for the  $\text{Ca}^{2+}$  entering the ikaite structure [13,14]. This promoted a model in which the ikaite columns are formed by mixing of groundwater with seawater that in turn leads to ikaite precipitation. As the issuing groundwater has a much lower salinity (and therefore lower density) than the surrounding seawater into which it flows, the columns grow upwards [13,14]. Indeed, when the divers cut or drilled into columns, the growth of new ikaite was seen instantaneously. Column growth rates of 40–50 cm/year were calculated from year on year measurements of fresh ikaite growth from cut columns [13,14]. Laboratory experiments simulating Ikka Fjord confirmed the model of groundwater-seawater mixing leading to ikaite precipitation. The results showed that ikaite forms when mixing a sodium carbonate solution of pH 9.9–10.6 with seawater, independent of whether the seawater source is natural or synthetic [9]. Ikaite was the main or only phase forming in experiments carried out at  $5^{\circ}\text{C}$ , whereas increasing amounts of nesquehonite ( $\text{Mg}(\text{HCO}_3)(\text{OH})\cdot 2\text{H}_2\text{O}$ ) and an amorphous phase co-precipitated at 10 and  $15^{\circ}\text{C}$ . At  $20^{\circ}\text{C}$ , only the amorphous phase was present, most likely amorphous calcium carbonate (ACC) [9].

When performing PhreeqC geochemical modelling of both the real water mixing in Ikka Fjord and of the laboratory experiments, it was seen that not only ikaite was saturated, but also calcite, aragonite, vaterite, monohydrocalcite and several Mg carbonates [9]. In the beginning of the Ikka project, it was assumed that, as orthophosphate is a well-known inhibitor of calcite [17,18], the presence of orthophosphate ions in the groundwater was the cause for ikaite precipitation in Ikka Fjord (see Table 1). However, the results of Stockmann et al. showed that the presence of phosphate ions was not mandatory to make ikaite precipitate as long as seawater was one of the mixing solutions [9]. On the other hand, when seawater was replaced with a 0.03 M  $\text{CaCl}_2$  solution to achieve ikaite saturation, calcite precipitated instead of ikaite unless either orthophosphate or  $\text{Mg}^{2+}$  ions were added [9]. Nielsen et al. found  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$  and  $\text{MgSO}_4^0$  ions in seawater to be effective inhibitors of calcite growth, especially when all three ions were present [19]. In experiments simulating ikaite precipitation in sea ice it was seen that when the ikaite precipitation was



taking place in seawater or at high pH (11), no phosphate was needed to inhibit calcite growth [20,21,22]. These authors suggested the  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  ions in seawater favour ikaite precipitation and inhibit calcite [19,20,21], supported by the results of Nielsen et al. [19]. The hypothesis concerning the role of  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  ions' in the precipitation of ikaite was tested in laboratory experiments, the results of which are presently in a manuscript, accepted for publication, but has not yet been published [23].

Another important factor controlling ikaite precipitation is the relative degree of saturation with respect to ikaite, calcite and other  $\text{CaCO}_3$  phases. When solutions are supersaturated with respect to all hydrous and anhydrous  $\text{CaCO}_3$  phases, ikaite precipitation is favoured [9,24]. In fact, in general supersaturated solutions are seen to favour precipitation of metastable phases [25], and ikaite is always present as a metastable phase [5]. Kinetic factors make ikaite precipitation favourable over all the other thermodynamically stable calcium and magnesium carbonates in a seawater environment at low temperatures ( $< 10^\circ\text{C}$ ), e.g., due to the ion speciation of the solution related to the degree of saturation (Fig. 4), and the solubility of ikaite at low temperatures [9]. Opposite to all other  $\text{CaCO}_3$  phases, ikaite becomes less soluble with decreasing temperature, and therefore ikaite precipitation is favoured by low temperature [6].

The geochemical modelling results of ion speciation when mixing groundwater with seawater in Ikka Fjord, is shown in Fig. 4. This depicts the dominant Ca ion species to be  $\text{CaCO}_3^0$ , when mixing solutions up to 60% groundwater with 40% or less seawater. The  $\text{CaCO}_3^0$  ion in solution surrounded by  $\text{H}_2\text{O}$  molecules resembles the ikaite structure, and it is therefore likely that minimal energy is required by the system to precipitate ikaite [9,14]. What can also be seen from Fig. 4, is the much higher  $[\text{Mg}]_{\text{tot}}$  compared to  $[\text{Ca}]_{\text{tot}}$ , which suggests that Mg carbonates could potentially form. However, XRD results confirm the ikaite columns and the ikaite from the experiments at  $5^\circ\text{C}$  to be either pure ikaite or ikaite with trace amounts of other carbonates (e.g., nesquehonite, calcite, aragonite, and vaterite) [9,13,14]. Thus, the conditions found in Ikka Fjord today do not favour Mg carbonate formation, but if seawater temperature was to increase, hydrous Mg carbonate phases like nesquehonite could become more favourable [9].

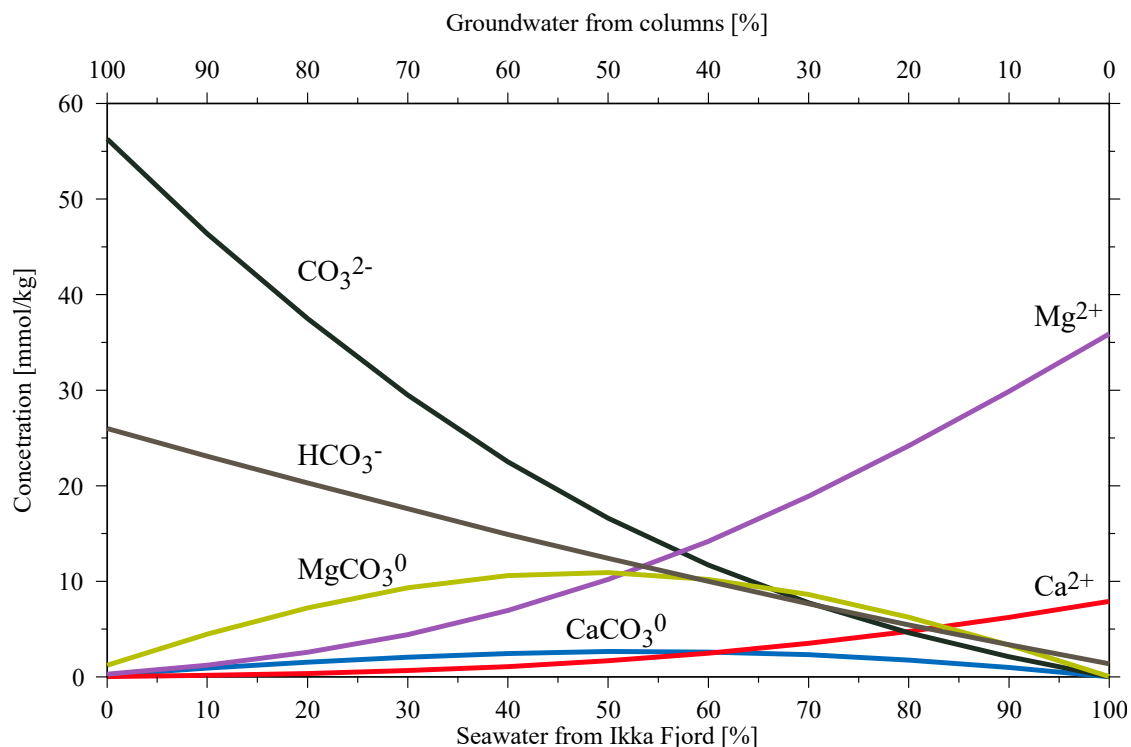


Fig. 4. Ion speciation distribution of groundwater-seawater mixing in Ikka Fjord. Modified from Stockmann et al. [9].

A harsh Arctic environment at Ikka Fjord, dominated by strong waves at times, large tidal shifts and extensive sea ice coverage in the winter, has induced some speculation as to how the relatively fragile ikaite columns can be so well-preserved? Whereas, calcite sits on saturation in pure Ikka Fjord seawater, ikaite is in fact undersaturated and should therefore theoretically dissolve [9], but it clearly does not. Trampe et al. found that cyanobacteria and diatoms are inhabiting the interior outermost 2-3 cm of the ikaite columns and covering the ikaite crystals together with secreted EPS, creating microbial biofilm, as seen on Fig. 5 [26,27]. From their studies, these authors suggested that the bacterial biofilm could in fact be producing a “glue” that enforces the connection between ikaite crystals, and are crucial for the large ikaite structures seen in Ikka Fjord [26,27]. Microorganisms and biofilms have been investigated as part of carbon capture and storage (CCS) studies for their role in enhancing the rate of capturing carbon [28,29,30]. Therefore they are also of interest for the ikaite precipitation mechanism, which is currently being explored in new experiments.

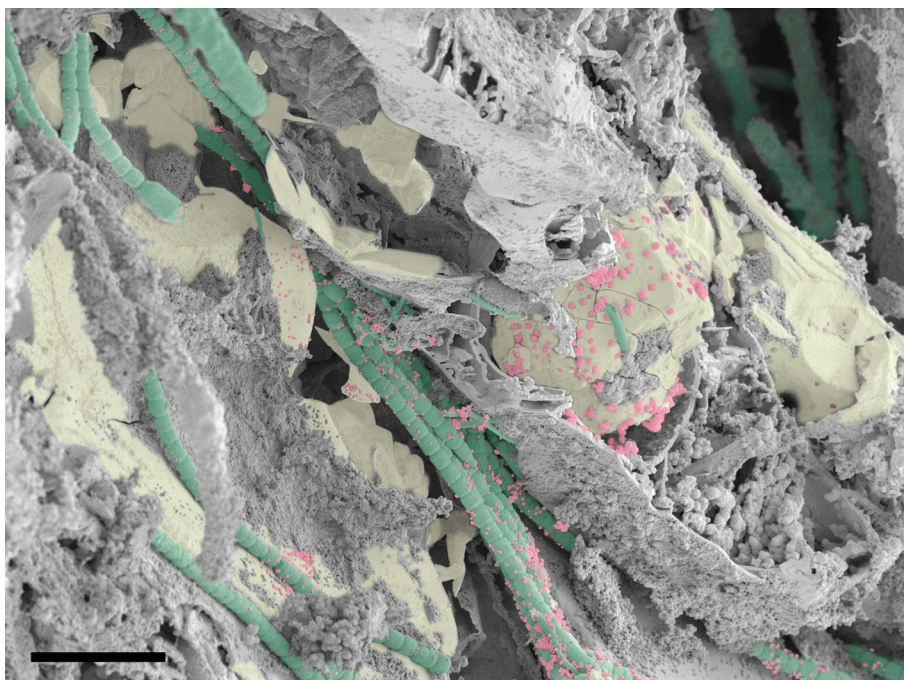


Fig. 5. Image: Erik Trampe. Cryo Scanning Electron Microscopy (SEM) image showing ikaite crystals (light yellow) covered with cyanobacteria (green), bacterial cells (pink) and collapsed biofilm/exopolymeric material (EPS) in grey. Scalebar represents 25 $\mu$ m. The colors are imposed on the image in Photoshop. Modified from Trampe et al. (2017) [26].

At present, a main obstacle for using ikaite for industrial carbon mineral storage is the high pH needed for ikaite precipitation. The findings of laboratory experiments carried out thus far by different research groups' [9,20,21,22,31] indicate that ikaite precipitation is favoured at a pH above 8-9. Purgstaller et al. succeeded in forming ikaite at conditions as low as pH 8.3 through mixing various (Ca,Mg)Cl<sub>2</sub> solutions with a 0.1 M NaHCO<sub>3</sub> solution at temperatures of 6 and 12°C [31]. They also showed that when transforming, ikaite ended up as one of the three CaCO<sub>3</sub> polymorphs depending on the [Mg<sup>2+</sup>]/[Ca<sup>2+</sup>] ratio of the reactive solution and on the temperature difference between the temperature of ikaite formation and that of transformation under air exposure. The largest temperature difference ( $\Delta T=19^{\circ}\text{C}$ ) led to the transformation of ikaite into calcite-vaterite mixtures under air exposure, whereas a smaller temperature difference ( $\Delta T=13^{\circ}\text{C}$ ) led to pure calcite [31]. At a [Mg<sup>2+</sup>]/[Ca<sup>2+</sup>] ratio  $\geq 14$  in solution, ikaite crystals kept in this solution at 20°C was transformed into aragonite due to excess aqueous Mg<sup>2+</sup> ions inhibiting calcite and vaterite formation [31].

From experimental work related to the CarbFix project in Iceland [32], it is known that when dissolving CO<sub>2</sub> gas in seawater instead of groundwater, more seawater is needed for the dissolution of CO<sub>2</sub> [33]. This leads to a CO<sub>2</sub>-charged solution of low pH and in order to reach favourable ikaite precipitation conditions, the solution pH has to increase significantly. However, knowing that ikaite can form naturally not only in Ikka Fjord but also in sea ice means



there is a chemical reaction where seawater is interacting with the carbon system of the ocean-ice-atmosphere leading to ikaite precipitation [3,4,34]. More experiments are therefore called for to understand these naturally occurring carbonate-forming processes at low temperature.

#### 4. Conclusion

The mineral ikaite has been shown both by observations in nature and from laboratory experiments to precipitate readily and instantaneously when mixing a carbonate-bearing solution with cold seawater. Ikaite is favoured by low temperature ( $< 10^{\circ}\text{C}$ ), a high degree of supersaturation with respect to calcium carbonate phases,  $\text{pH} > 8\text{--}9$ , and by possibly  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$  and  $\text{MgSO}_4^0$  ions in seawater acting as inhibitors of calcite growth. Even when a multitude of Ca and Mg carbonate minerals are saturated, metastable ikaite is often seen as the only carbonate phase forming, illustrating the low energy needed of a system to precipitate this mineral. When becoming unstable at higher temperatures, ikaite breaks down into one or more of the  $\text{CaCO}_3$  phases, calcite, aragonite, or vaterite, but without losing its carbonate content. Hence, ikaite could potentially offer an effective CCS method in a cold seawater environment.

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#### References

- [1] Rink Hinrich J. “Eskimoiske Eventyr og Sagn” Copenhagen (1866).
- [2] Pauly Hans. “Ikaite”, a new mineral from Greenland” *Arctic* 16 (1963): 263–64.
- [3] Dieckmann Gerhard Stephan, Gernot Nehrke, Stathys Papadimitriou, Joerg Göttlicher, Ralph Steininger, Hilary Kennedy, Dieter Wolf-Gladrow, and David N. Thomas. “Calcium carbonate as ikaite crystals in Antarctic sea ice” *Geophysical Research Letters* 35 (2008): L08501, doi: 10.1029/2008GL033540.
- [4] Dieckmann Gerhard Stephan, Gernot Nehrke, Christiane Uhlig, Joerg Göttlinger, Sebastian Gerland, Mats A. Granskog, and David N. Thomas. “Brief communication: ikaite ( $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ) discovered in Arctic sea ice” *Cryosphere* 4 (2010): 227–30.
- [5] Marland Greg. “The stability of  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  (ikaite)” *Geochimica et Cosmochimica Acta* 39 (1975): 83–91.
- [6] Bischoff James L., John A. Fitzpatrick, and Robert J. Rosenbauer. “The solubility and stabilization of ikaite ( $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ) from  $0^{\circ}\text{C}$  to  $25^{\circ}\text{C}$ : environmental and paleoclimatic implications for thinolite tufa” *The Journal of Geology* 101 (1993): 21–33.
- [7] Dahl Karsten, and Bjørn Buchardt. “Monohydrocalcite in the Arctic Ikka fjord, SW Greenland: first reported marine occurrence.” *Journal of Sedimentary Research* 76 (2006): 460–71.
- [8] Hansen Marc Overgaard, Bjørn Buchardt, Michael Kühl, and Bo Elberling. “The fate of the submarine ikaite tufa columns in southwest Greenland under changing climate conditions” *Journal of Sedimentary Research* 81 (2011): 553–561.
- [9] Stockmann Gabrielle, Elin Tollefsen, Alasdair Skelton, Volker Brüchert, Tonci Balic-Zunic, Jörgen Langhof, Henrik Skogby, and Andreas Karlsson. “Control of a Calcite inhibitor (phosphate) and Temperature on Ikaite precipitation in Ikka Fjord, Southwest Greenland” *Applied Geochemistry* 89 (2018): 11–22, doi: 10.1016/j.apgeochem.2017.11.005.
- [10] Upton Brian G. “Tectono-magmatic evolution of the younger Gardar southern rift, South Greenland” *Geological Survey of Denmark and Greenland Bulletin* 29, Copenhagen (2013).
- [11] Emeleus Charles Henry. “The Grønnedal-Ika Alkaline Complex” *Meddelelser om Grønland* 186, South Greenland, Copenhagen (1964).
- [12] Seaman Paul, and Bjørn Buchardt. “The Columns of Ikaite Tufa in Ikka Fjord, Greenland” *Monographs of Greenland*, Copenhagen, Danish Polar Center (2006).

- [13] Buchardt Bjørn, Paul Seaman, Gabrielle Stockmann, Marie Vous, Uffe Wilken, Lene Düwel, Aase Kristiansen, Chris Jenner, Michael J. Whitticar, Reinhardt Møbjerg Kristensen, Godtfred Høpner Petersen, and Lone Thorbjørn. “Submarine columns of ikaite tufa” *Nature* 390 (1997): 129–30.
- [14] Buchardt Bjørn, Carsten Israelsson, Paul Seaman, and Gabrielle Stockmann. “Ikaite tufa towers in Ikka Fjord, Southwest Greenland: their formation by mixing of seawater and alkaline spring water” *Journal of Sedimentary Research* 71 (2001): 176–89.
- [15] Ranta Eemu. “Study of Opaque Phases in Carbonatites of the Grønødal-ika Alkaline Complex, Southwest Greenland” *B.Sc. thesis in Geology* (2015), Stockholm University, Stockholm.
- [16] Ranta Eemu. “Fluid-rock Reactions in the Carbonatites of the Grønødal-ika Alkaline Complex, South Greenland” *M.Sc. thesis in Geology* (2017), University of Helsinki, Helsinki.
- [17] Burton Elizabeth A., and Lynn M. Walter. “The effect of orthophosphate on carbonate mineral dissolution rates in seawater” *Chemical Geology* 56 (1986): 313–23.
- [18] Burton Elizabeth A., and Lynn M. Walter. “The role of pH in phosphate inhibition of calcite and aragonite precipitation rates in sea water” *Geochimica et Cosmochimica Acta* 54 (1990): 797–808.
- [19] Nielsen Morten R., Karina K. Sand, Juan Diego Rodríguez-Blanco, Nicolas Bovet, Johanna Generosi, Kim Dalby, and Susan L. Stipp. “Inhibition of calcite growth: combined effects of  $Mg^{2+}$  and  $SO_4^{2-}$ ” *Crystal Growth & Design* 16 (2016): 6199–6207.
- [20] Hu Yubin, Dieter A. Wolf-Gladrow, Gerhard Stephan Dieckmann, Christoph Völker, and Gernot Nehrke. “A laboratory study of ikaite ( $CaCO_3 \cdot 6H_2O$ ) precipitation as a function of pH, salinity, temperature and phosphate concentration” *Marine Chemistry* 162 (2014): 10–18.
- [21] Hu Yubin, Gerhard Stephan Dieckmann, Dieter A. Wolf-Gladrow, and Gernot Nehrke. “Laboratory study on coprecipitation of phosphate with ikaite in sea ice” *Journal of Geophysical Research: Oceans* 119 (2014): 7007–15.
- [22] Hu Yubin, Mariette Wolthers, Dieter A. Wolf-Gladrow, and Gernot Nehrke. “Effect of pH and phosphate on calcium carbonate polymorphs precipitated at near-freezing temperature” *Crystal Growth & Design* 15 (2015): 1596–1601.
- [23] Tollefsen Elin, Gabrielle Stockmann, Alasdair Skelton, Carl Magnus Mørth, Christoph Dupraz, and Erik Sturkell. “Chemical controls on ikaite formation” *Mineralogical Magazine, accepted manuscript* (2018), doi: 10.1180/mgm.2018.110.
- [24] Johnston John, H. E. Merwin, and E. D. Williamson. “The several forms of calcium carbonate” *American Journal of Science -Fourth Series* 41(246) (1916): 473–93.
- [25] Mangin Denis, François Puel, and Stéphane Veesler. “Polymorphism in processes of crystallization in solution: a practical review” *Organic Process Research & Development* 13 (2009): 1241–53.
- [26] Trampe Erik C., Jens E. Larsen, Mikkel Andreas Glaring, Peter Stougaard, and Michael Kühl. “In situ dynamics of  $O_2$ , pH, light, and photosynthesis in ikaite tufa columns (Ikka Fjord, Greenland) – a unique microbial habitat” *Frontiers in Microbiology* 7 (2016), doi: 10.3389/fmicb.2016.00722.
- [27] Trampe Erik C., Richard W. Castenholz, Jens E. Larsen, and Michael Kühl. “Phototrophic microbes form endolithic biofilms in ikaite tufa columns (SW Greenland)” *Environmental Microbiology* 19(11) (2017): 4754–70
- [28] Mitchell Andrew C., Adrienne J. Phillips, Randy Hiebert, Robin Gerlach, Lee H. Spangler, and Alfred B. Cunningham. “Biofilm enhanced geologic sequestration of supercritical  $CO_2$ ” *International Journal of Greenhouse Gas Control* 3 (2009): 90-9, doi: 10.1016/j.ijggc.2008.05.002.
- [29] Mitchell Andrew C., Knud Dideriksen, Lee H. Spangler, Alfred B. Cunningham, and Robin Gerlach. “Microbially Enhanced Carbon Capture and Storage by Mineral-Trapping and Solubility-Trapping” *Environmental Science & Technology* 44 (2010): 5270-76, doi: 10.1021/es903270w.
- [30] Cunningham Alfred B., Robin Gerlach, Lee H. Spangler, and Andrew C. Mitchell. “Microbially enhanced geologic containment of sequestered supercritical  $CO_2$ ” *Energy Procedia* 1 (2009): 3245-52, doi: 10.1016/j.egypro.2009.02.109.
- [31] Purgstaller Bettina, Martin Dietzel, Andre Baldermann, and Vasileios Mavromatis. “Control of temperature and aqueous  $Mg^{2+}/Ca^{2+}$  ratio on the (trans-)formation of ikaite” *Geochimica et Cosmochimica Acta* 217 (2017), doi: 10.1016/j.gca.2017.08.016.
- [32] Matter Jürg M., Martin Stute, Sandra Ósk Snæbjörnsdóttir, Eric H. Oelkers, Sigurdur R. Gislason, Edda Sif Aradóttir, Bergur Sigfusson, Ingvi Gunnarsson, Holmfríður Sigurdardóttir, Einar Gunnlaugsson, Gudni Axelsson, Helgi A. Alfredsson, Domenik Wolff-Boenisch, Kiflom Mesfin, Diana de la Reguera Fernandez, Jennifer Hall, Knud Dideriksen, and Wallace S. Broecker. “Rapid carbon mineralization for permanent and safe disposal of anthropogenic carbon dioxide emissions” *Science* 352 (2016): 1312-14.
- [33] Wolff-Boenisch Domenik. “On the buffer capacity of  $CO_2$ -charged seawater used for carbonation and subsequent mineral sequestration” *Energy Procedia* 4 (2011): 3738-45.
- [34] Hu Yubin, Feiyue Wang, Wieter Boone, David Barber, and Søren Rysgaard. “Assessment and improvement of the sea ice processing for dissolved inorganic carbon analysis” *Limnology and Oceanography Methods* 16 (2018): 83–91, doi: 10.1002/lom3.10229.